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The Source and Nature of the Earth's Primitive Atmosphere.

The Earth's Atmosphere seems to be different from the other planetary atmospheres in possessing a large amount of free oxygen. As Stoney (1) originally pointed out, the existing atmosphere of any planet will depend, not only on the elements which may have been originally present, but also on the temperature and gravitational potential of the planet, the lighter atoms tending to escape as the temperature increases or the potential diminishes. Jeans (2) and others have obtained expressions for the rate of escape of any gaseous molecule for given values of the temperature and gravitational potential, and in a general way, our knowledge of the planetary atmospheres is in agreement with their conclusions.

It has, however, been recognised for many years that it is highly improbable that the original atmosphere of the earth could have contained any free oxygen. Apart from the inner core of the earth, which usually is considered to consist of metallic iron (3), its outer layers are sub-oxidised to such an extent that they would easily be capable of combining with all the oxygen contained at present in the atmosphere. It was therefore usually concluded that the atmosphere of the earth previous to the solidification of the crust consisted mainly of CO_2, a very large amount of H_2O, since the oceans were all in the gaseous state, and the existing amounts of nitrogen and argon. This atmosphere was considered primary, in the sense that its constituents had always been in the gaseous state from the formation of the earth, and this obviously put a limit to the possible initial temperature of the planet.

Jeffreys (4), however, proposed about 1924 that the earth had lost all its original atmosphere, and that a secondary atmosphere was formed by the escape of gases, including all the oceanic water, from the outer crust during solidification. Brown (5) has recently confirmed this theory by investigations on the cosmical and terrestrial abundances of the noble gases, neon, argon, etc. He concluded that the major atmospheric constituents, water, nitrogen, oxygen, and carbon dioxide, were not retained in any appreciable amount as gases during the process of earth formation, and, consequently, must have been retained chemically and subsequently released from the cooling earth to form the primitive atmosphere. It might be thought that the presence of argon in the existing atmosphere was contrary to this view, since argon is so chemically

inert that we could hardly imagine it having been retained chemically, and as its molecular weight is slightly less than CO_2 it should, therefore, have escaped. Atmospheric argon, however, consists to about 99·5% of the isotope A^{40}, which is produced by electron capture of the radioactive potassium isotope K^{40}. This process seems to be capable of producing all the A^{40} at present in the atmosphere (6), and hence the apparent discrepancy is explained.

This view of the method of formation of the primitive atmosphere only confirms the hypothesis that it contained no free oxygen. Volcanoes are known to emit hydrogen, carbon dioxide, water vapour, and nitrogen, but practically no oxygen; and it seems unlikely that if oxygen was originally held chemically by the surface materials, it could ever be liberated again in the free state. It does, however, rather complicate our ideas about the state of the atmosphere before the formation of the earth's surface crust. It was previously held that before the surface crust of the earth cooled to the critical temperature of water (critical temperature, 647°K. critical pressure, 218 atmospheres) all the ocean water was present as gas in the atmosphere. This would mean that the atmospheric pressure at this period would have been of the order of 300 atmospheres. This estimate may, however, be incorrect if we adopt Jeffrey's view that the water of the hydrosphere was emitted during the solidification of the outer silicious crust of the earth, since the maximum pressure depends on how this solidification took place. According to our present knowledge, the earth consists of three principal layers, the crust, the mantle, and the core. We are here mainly concerned with the crust only, which consists of at least two comparatively thin subsidiary layers which may be roughly distinguished as a superficial granitic layer of mean thickness of about 11 km., density 2·65g. /c.c. and below this a mainly basaltic layer of thickness 24 km. and density 2·87g. /c.c. It has been pointed out by Lord Kelvin and others that if the melting point versus pressure gradient for a material exceeds the adiabatic gradient for the liquid phase, then the liquid on cooling will solidify from the bottom upwards. This condition seems to be satisfied for the mantle of the earth, which is now considered to consist mainly of olivine (3), and it is usually considered that it is also true for the crust. This entails that the surface of the crust would remain liquid at a temperature of —say—1500°K. till its solidification was complete, and, presumably, most of the water of the hydrosphere and other gases had been emitted to form an atmosphere. Since the temperature of this atmosphere would initially be far above the critical temperature of water, the pressure at this stage would be of about the order of 300 atmospheres, as originally held. Once the crust was solidified, and convection currents in it had ceased, its cooling to the critical temperature of water would be very rapid, perhaps a period of a few years. This point is considered more fully later.

An alternative view should perhaps be considered. The material of the crust cannot really be justly treated as though it were a homogenuous crystalline material. It seems quite possible that during its solidification a superficial solid crust or slag might form on its surface, this crust being composed of lighter and more infusible material than the bulk of the crust. It is well known from practical experience with

lava flows, etc., that the presence of such a solid outer layer reduces enormously the heat flow from the interior liquid material owing to the comparatively low heat conductivity of the solid layer. Thus, the solidification of the lower layers of the crust would be greatly retarded, and the rate of emission of the primitive atmosphere correspondingly reduced. It is also highly probable that the surface of the upper solid layer would rapidly fall below the critical temperature of water, and that, consequently, the pressure of the primitive atmosphere might never approach 300 atmospheres, the formation of the ocean being more or less a continuous process depending on the rate of emission of water vapour from the slowly solidifying liquid portion of the crust, the crustal gases being assumed to escape through fissures in the upper solid floating layer. Later, it will be seen that this idea of the mode of formation of the primitive atmosphere would tend to invalidate Tammann's theory of the origin of atmospheric oxygen.

It follows also from this theory that we may now definitely reject the idea that the primitive atmosphere contained any large amount of methane. In a previous paper (8), in order to explain the apparent excess of free carbon in the lithosphere, I considered this possibility. As the earth was assumed to have been able to retain H_2O vapour of molecular weight 18, from its original formation, it seemed likely that it could also have retained CH_4 of molecular weight 16. Methane is apparently one of the principal constituents of the atmospheres of the major planets, and might accordingly also have been present in the earth's atmosphere if this were considered to be a primary, not a secondary, one. It now seems clear that the earth must have lost all its original methane, except it had been chemically retained like the other secondary atmospheric constituents. This seems highly improbable, and I think the methane hypothesis is certainly incorrect.

Therefore, I think we may safely conclude that the primitive atmosphere, as originally emitted from the cooling crust, consisted mainly of H_2O, CO_2 and N_2, but contained no O_2. The maximum pressure reached by the resulting atmosphere cannot be fixed, since, as has already been shown, it depends on how the crust solidified. Three explanations of the subsequent production of free oxygen have been given. They are :—

(A) Photosynthetic reduction of CO_2 by biological processes.

(B) Thermal dissociation of H_2O at high temperatures, and subsequent escape of H_2 (9).

(C) Photochemical dissociation of H_2O by U.V. light, and subsequent escape of H_2 (8).

(A) The Photosynthetic Reduction of CO_2.

Most geologists consider that the main bulk of atmospheric oxygen has been produced by the first process, which is, apparently, more than capable of supplying all the present atmospheric oxygen as well as the oxygen consumed by the sedimentary rocks during their formation from igneous rocks. This means that a total quantity of CO_2 of the order of 10 kg. per cm^2 must have been present in the primitive

atmosphere, or, conceivably, may have escaped continuously from the crust during geological ages, being simultaneously removed by photosynthesis so that the pressure of CO_2 was never very large. The figure for the total CO_2 is based on Goldschmidt's (10) estimates for the carbonates in the sedimentary rocks, and the free carbon in the shales, coal, etc. The reduction of this amount of CO_2 would furnish a super-abundant supply of oxygen, but I have already discussed this point fully in the previous paper (8).

It seems clear, however, that this process could not have started in an atmosphere with no free oxygen. It is true that during active photosynthesis, the biological agent absorbs CO_2, and releases oxygen ; but during periods of insufficient illumination, it oxidises carbon to CO_2 to supply its life processes with the necessary energy.

Thus, we can hardly imagine the process starting without some initial free oxygen. Furthermore, the part of the solar spectrum absorbed by the ozone layer in the existing atmosphere seems to be lethal to most forms of life, which would apparently involve that such a layer must be formed before photosynthesis could start. This argument is perhaps not as cogent as the previous one, since we can easily conceive that the primitive organisms may have been immune to the wave-lengths concerned, and that their descendants lost this immunity owing to it being no longer required. We are, however, forced to conclude that some oxygen at least must have been first supplied by some non-biological process such as Tammann's thermal dissociation or my own photochemical theory.

(B) The Thermal Dissociation Theory.

Tammann's theory was put forward in 1924, and, consequently, is based on the idea that the atmosphere of the earth was of primary origin. He assumes that while the molten earth was cooling, all the water of the hydrosphere was present in the atmosphere, giving a pressure of about 100 atmospheres due to the water vapour alone. At the then existing surface temperature of the earth, a certain percentage of the atmospheric water vapour would be thermally dissociated into hydrogen and oxygen and, since the hydrogen would rapidly escape into space, a surplus of free oxygen would remain behind. He, probably correctly, considers that as long as the surface of the earth was liquid, any surplus oxygen would be taken up by the sub-oxidised materials of the crust and that it was only subsequent to the formation of a solid crust that free oxygen could accumulate in the atmosphere. He concluded that by this process an amount of free oxygen, about equal to that at present in the atmosphere, would have been produced.

Goldschmidt has objected to Tammann's theory on the grounds that it does not account for the oxygen which has been absorbed in the formation of the sedimentary rocks during geological time. He estimates that this amounts to between 1·1 and 2·4 times the existing atmospheric oxygen. It is true that Tammann's estimate of an original water vapour pressure of 100 atmospheres is, however, rather

conservative, as according to Goldschmidt's figures the pressure would be about 270 atmospheres if the present ocean were evaporated. If this pressure is adopted, the process is perhaps capable of supplying enough oxygen, but Goldschmidt holds that it supplied only enough oxygen to enable the main biological reduction of CO_2 to start. The majority of geologists would, I think, agree with Goldschmidt that most of the atmospheric oxygen must have been produced from CO_2, since this view agrees much better with the amount of free carbon of presumably organic origin, present in the lithosphere.

There are two other points about Tammann's theory which the author has not considered. These are :—

(a) The time available for the escape of hydrogen.

(b) The temperature of the outer layers of the postulated water vapour atmosphere, if its ground level temperature was 1500°K. The rate of escape of hydrogen will depend on this temperature and not directly on the ground level temperature.

It is easier perhaps to consider these two problems separately, as far as is possible.

(a) *Time available for the escape of hydrogen.*—Tammann (9) seems to consider that the period from the formation of the earth as a ball of gas to the solidification of its outer crust was comparable with geological time. This is incorrect. Jeffreys (11) has shown that the solid crust would form about 15,000 years after the formation of the earth, and, furthermore, he concludes that the time from the solidification of the crust to the condensation of the ocean was comparable with that needed for a red hot coal to become capable of being handled (*loc. cit.*, p. 148). It is only during this period that Tammann assumes that the hydrogen, necessary to explain the existence of free oxygen, escaped.

To arrive at any accurate estimate of the length of this period is probably impossible. It depends both on how the crust was formed and also on the rate of loss of heat of the postulated water atmosphere. This heat loss was supplied by (a) the cooling of the atmosphere and (b) the cooling of the surface materials of the earth. Of these two sources, it seems probable that the first is the most important, since the low thermal conductivity of the solid crust would very quickly reduce the heat flow to the surface to a value small compared with the probable rate of loss of heat from the atmosphere.

Tammann is not very clear as to the exact method in which he assumes the crust of the earth solidified. He seems to assume a period during which the atmosphere was protected from the lower reducing layers of the crust by an upper solid layer, followed by a rapid cooling of the atmosphere as the solid crust thickened. The formation of free oxygen is supposed to have occurred in the first period mainly when the temperature is assumed to have remained at 1500°C. The best way to meet these requirements is to imagine that the original upper solid crust consisted of lighter, higher melting point materials which floated on a heavier still liquid layer. Even under these conditions the first period will practically not exist, the

rate of cooling of the atmosphere depending nearly entirely on its own original heat-content, which would be large, as the present mass of water per cm.^{2} of the earth's surface is about 280 kg.

Let us assume that the earth at this stage lost heat by radiation like a black body. Since Tammann has assumed that the temperature of the atmosphere was 1500°K. at all heights, and water vapour possesses a rich infra-red spectrum, it seems justifiable to assume that the effective radiation temperature at any instant would be the same as the atmospheric temperature. It is clear that once a solid upper crust has formed on the lower liquid layer, the temperature of the atmosphere must at once start to fall below the assumed melting point temperature of 1500°K, since for any heat to escape from the liquid there must be a temperature gradient across the solid upper layer. Suppose we try to estimate the thickness of the crust when the atmospheric temperature has fallen to 1000°K., assuming that say 50% of the total heat loss is supplied from the lower liquid layer by thermal conduction. Let x = thickness of crust. Then we have :—

$$\tfrac{1}{2}\,\sigma\theta^4 = \frac{K\,(\theta_0 - \theta)}{x}$$

Where : σ = Stefan's constant
$= 1{\cdot}37 \times 10^{-12}$ cal. cm^{-2} sec^{-1} degree^{-4}
K = thermal conductivity
$= {\cdot}01$ cal. cm^{-1} sec^{-1} degree^{-1}
θ_0 = temperature of liquid layer $= 1500$°K.
θ = temperature of atmosphere $= 1000$°K.

This gives $$x = \frac{2 \times 10^{-2} \times 500}{1{\cdot}37 \times 10^{-12} \times 10^{12}} \text{ cm.}$$
$$= 7{\cdot}3 \text{ cm.}$$

This result may appear to be surprisingly small, but agrees fairly well with our experience of the amount of thermal insulation required for a furnace. I think the result shows conclusively that in considering the cooling of the water vapour atmosphere, after the solid crust is formed, we may completely neglect the heat supplied through the crust, and consider the heat-content of the atmosphere only.

It is not very difficult to deal with this problem more accurately, if we assume an isothermal atmosphere losing heat like a black body.

Let

m = mass of atmosphere per cm^2
$= 2{\cdot}8 \times 10^5$/g
s = specific heat of atmosphere
$= 0{\cdot}5$ cal. per g. per degree
θ_0 = initial temperature of atmosphere
$= 1500$°K.
θ = temperature at time t

Then we have :—

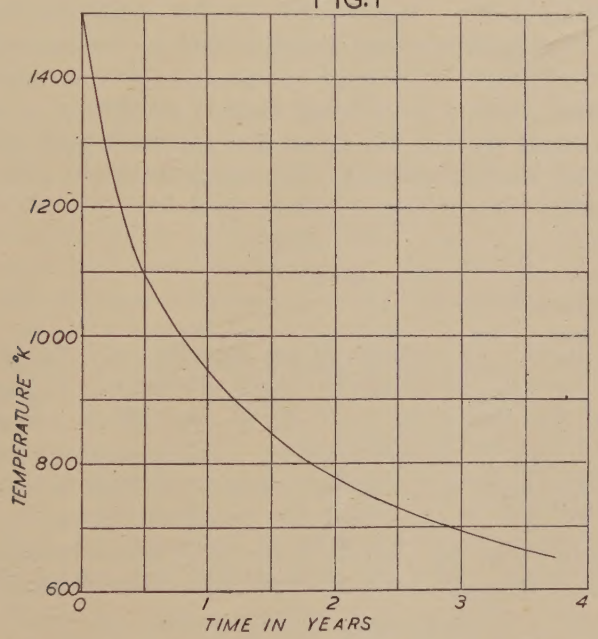
$$\sigma\theta^4 = -\text{ ms. } \frac{d\theta}{dt}$$

which gives :—

$$t = \frac{ms}{3\sigma}\left(\frac{1}{\theta^3} - \frac{1)}{\theta_o^3}\right) \text{ sec.}$$

I have plotted the results of this expression in Figure 1. This shows how rapid the cooling of the atmosphere would be on these assumptions. The temperature falls from 1500°K. to 1000°K. in about 9 months, and to the critical temperature of water, 647°K., in about 3·75 years, when the ocean would commence to form ; the critical pressure of water being 218·5 atmospheres, and, thus, considerably less than the assumed atmospheric pressure of about 270 atmospheres due to water vapour alone. It is probable that the values obtained are too small, as it is unlikely that the water vapour would behave as a black body, but, at least, they show that the time of cooling would be short, being of the order of years only.

FIG. 1



This is not, however, a fundamental objection to Tammann's theory. If we take Jeans' (12) approximate expression for the time of escape of any component gas of an isothermal atmosphere :—

$$t_1 = \frac{1{\cdot}45C}{g(1 + 3ga/C^2)} \quad \text{exp. } 3ga/C^2$$

where t_1 = time of escape ; C = molecular velocity of component gas ; g = gravitational acceleration, and a = radius of planet. We find that for molecular hydrogen, at a temperature of 1500°K., the time of escape would be only about 15 days

Milne (13) and Jones (14) have carried out more elaborate investigations of the problem, but their results are essentially the same, if t_1 is taken as the time required for the density of the gas to fall to 1/e of its original value and not to zero as Jeans originally assumed. This correction would be of no importance, since in any case only very approximate estimates can be made owing to the great uncertainty of the actual conditions. I think, therefore, that if the atmosphere is assumed to be isothermal there would be sufficient time, after the solidification of the crust, and during the cooling, of the atmosphere for enough hydrogen to escape to leave a considerable amount of free oxygen in the primeval atmosphere. If the atmosphere is not assumed to be isothermal, both the time of cooling and the rate of escape of hydrogen will be altered. This problem is considered in the following section.

(b) *Temperature of outer layers of original water vapour atmosphere.*—Tammann's assumption that the temperature of the top layers of the water vapour atmosphere on which the rate of escape of hydrogen would depend, was of the same order as the surface temperature of the earth's crust at the time, seems to be the most uncertain point in his theory. Milankovitch (15) has considered the problem of the rate of change of temperature with height in such an atmosphere, and concludes that when the temperature of the crust was about 1200°C., its approximate melting point, a permanent layer of cloud would exist at a height of about 200 km. at a temperature of about 100°C. He shows that the mechanical equilibrium of this atmosphere would be indifferent, i.e. that the temperature gradient with height would be the adiabatic gradient, which is equal to :—

$$\frac{Mg.}{R}\,\frac{\gamma - 1}{\gamma} \quad \text{where,}$$

M = molecular weight ; R = universal gas constant ; g = the gravitational constant ; and γ = the ratio of the specific heats. Taking $\gamma = 4/3$ for water vapour, the lapse rate in this atmosphere would be 1°C. per 188 m., which value is independent both of temperature and pressure. As the system gradually cools, the height of the cloud will decrease and its temperature increase as can easily be shown.

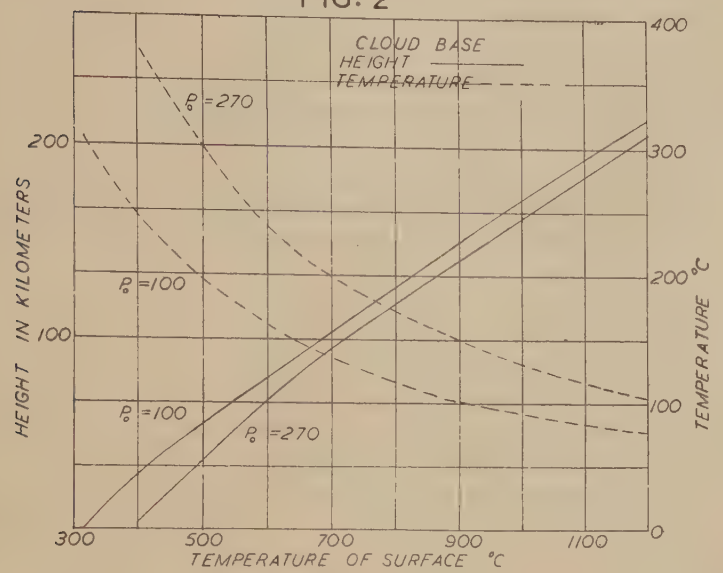
The cloud will form at the level in the atmosphere where the pressure is equal to the saturated vapour pressure of water at the existing temperature. If p is the pressure at any height, and θ the corresponding temperature, then we have :—

$$p = p_\circ(\theta/\theta_\circ)^{\gamma/(\gamma - 1)} = p_\circ(\theta/\theta_\circ)^4$$

where $p_\circ$ and $\theta_\circ$ are the values for zero height, and $\gamma = 4/3$. The value of $p_\circ$ is constant until the critical temperature of water, 374°C. is reached at the surface. The simplest way, therefore, to deal with this equation is to assume a certain value θ for the cloud temperature, when p will be equal to the saturated vapour pressure, and then obtain the surface temperature $\theta_\circ$ from the relation :—

$$\log \theta_\circ = \log \theta + (\log p_\circ - \log p)/4$$

FIG. 2



The height of the cloud is obviously equal to 188 $(\theta_o - \theta)$ metres, since the lapse rate is independent of θ_o. In Figure 2, I have plotted the temperature of the cloud and its height against the surface temperature, assuming that all the present ocean water was then present in the atmosphere, which gives p_o a value of about 270 atmospheres. It will be seen that, as already mentioned, the cloud temperature rises and its height decreases as the system cools. The maximum temperature the cloud could have would be the critical temperature, i.e., 374°C., but this would only occur when the surface temperature was about 400°C., and the thermal dissociation of the water vapour negligible. To show the effect of assuming a lower value for the original atmospheric pressure, I have also plotted the curves for $p_o = 100$ atmospheres. The change in them is not very striking. At any given surface temperature, the cloud temperature is lower and the cloud height greater than in the first case when p_o was taken equal to 270 atmospheres. The ocean will begin to form at a temperature of 312°C., at which pressure the saturated vapour pressure of water is 100 atmospheres. The cloud will then apparently be at ground level, and will have reached its maximum temperature of 312°C. It seems doubtful, however, that the postulated conditions should be carried to such an extreme case.

If Milankovitch's theory is correct, it would seem to disprove Tammann's theory of the origin of the free oxygen. It is difficult to imagine that the outer layers of the atmosphere above the cloud level could be at a considerably higher temperature than the cloud, and unless this were true the rate of escape of any hydrogen present would be excessively slow. It is true that the rate of cooling of the system would be reduced by the cloud layer, but it seems unlikely that this would compensate for the effect of the low temperature on the rate of escape. R. Wildt (16) considers that for the loss of molecular hydrogen to be complete in geological time, the tem-

perature must be greater than 250°C., and for it to be complete in a few years, greater than 850°C. ; and a cloud temperature of even 250°C. is only reached when the surface temperature has fallen to 570°C., and the period to the final formation of the ocean correspondingly reduced.

Milankovitch has neglected the effect of solar radiation on the postulated atmosphere, and it might be urged that this radiation could produce high temperatures in its upper layers, since it apparently does so in the F layers of the existing atmosphere. This effect is usually attributed to the layers in question being mainly composed of monatomic and diatomic molecules which are capable of gaining thermal energy from the ultra-violet solar radiation, but find it difficult to dispose of this energy due to the fact that they possess no infra-red spectra. This phenomenon should apparently not occur in an atmosphere mainly consisting of water vapour, which has a very rich infra-red spectrum, and which will radiate approximately as a grey body. I think, therefore, that it is justifiable to conclude that at no height in the water vapour atmosphere would the temperature start to increase again, as it seems to do in the existing atmosphere.

It may be questioned, however, whether it is justifiable to assume that the adiabatic lapse rate of temperature would persist to such great heights in the primitive atmosphere. The theory leads to some rather peculiar results. It seems reasonable to conclude that if the earth was totally enclosed by a dense layer of cloud at a certain temperature, that this layer would absorb practically all the heat radiation coming from below, and that consequently the rate of loss of heat by the earth as a whole would depend mainly on the cloud temperature. This leads to the strange paradox that the hotter the earth's surface is, the slower it cools ; the cloud temperature rising as the surface temperature falls. The effect of the decrease of the surface area of the cloud, as its height decreases, is not important, since the height of the cloud is always small compared to the radius of the earth. Milankovitch considers that an equation, due to Schwartzschild (17), applies to the primitive water vapour atmosphere. The equation is :—

$$\frac{d\theta}{dx} = \frac{-Mg}{4R} \cdot \frac{\theta^4 - \mu^4}{\theta^4}$$

where :—

θ = the temperature at a height x.
M = the molecular weight.
g = gratitational constant.
μ = temperature of the outer layer of the atmosphere.

He then assumes that μ^4 may be neglected in comparison to θ^4, and, consequently, obtains :—

$$\frac{d\theta}{dx} = -Mg/4R$$

This value is the same as the adiabatic lapse rate for a gas for which $\gamma = 4/3$ and, hence, he concludes that the primitive atmosphere would be in indifferent mechanical equilibrium.

It is doubtful whether it is correct to assume that μ^4 can be entirely neglected. As Jeans (2. p. 337) points out, there must be a limit in any atmosphere beyond which adiabatic equilibrium is impossible, and above this height an isothermal layer would exist. An atmosphere in convective equilibrium possesses a definite upper boundary at the height at which its temperature would be O°K. For the primitive atmosphere, where the lapse rate is 1°C. per 188 m., this height is 280 km. when the surface temperature is 1200°C. Such a condition is obviously impossible, since an atmospheric layer at O°K., would emit no radiation, while it would absorb both radiation coming from below and also solar radiation. It is, thus, clear that the isothermal layer, predicted by Jeans, must start at a lower level than the theoretical upper boundary of the convective atmosphere. It would seem justifiable to assume that the value of μ to be used should be the temperature of this isothermal layer, and it is this temperature that will control the rate of escape of hydrogen from the atmosphere. Now Milankovitch has entirely neglected the effect of solar radiation, and for a good heat absorber like water vapour one would be inclined to imagine that the temperature of the isothermal layer would be at least equal to the solar equilibrium temperature of say 280°K. This means that the lapse rate would continuously decrease with height in the atmosphere, and that the results obtained from the simple theory can only be approximately correct. From the point of view of the validity of Tammann's theory, the method is unsatisfactory; since we are to a certain degree begging the question, by assuming a low value for μ. On the whole, however, I think that there must have been a lapse rate of temperature in the primitive atmosphere, and probably that temperature of the outer layers of this atmosphere was too low to allow the hydrogen to escape rapidly; but further investigation of this problem is required.

In the previous discussion I have assumed, following Tammann, that a solid upper crust formed on top of a lower liquid layer during the final stages of the solidification of the earth. As already mentioned, many geologists consider that the outer crust solidified from the bottom upwards, so that the still liquid materials of the crust would be in contact with the primitive atmosphere until the whole crust was solid. It is only after the surface of the earth is solid, that Tammann considers free oxygen could be produced; but, as I have shown that the period from the formation of the upper crust to the condensation of the ocean depends nearly entirely on the heat-content of the water vapour atmosphere, this view of the mode of solidification of the earth would not reduce the possibility of the production of free oxygen by thermal dissociation.

In some ways, indeed, the solidification of the crust from below is more favourable to the theory than the former hypothesis. For the production of any considerable amount of free oxygen by thermal dissociation, an appreciable fraction of the present ocean water must have been present in the atmosphere when the surface solidified, since both the quantity of dissociated water vapour and also the time available for the escape of hydrogen depend on this quantity. Now, if a solid upper crust formed at an early stage over a liquid substratum, the cooling of this substratum would be slow, and the rate of emission of water vapour correspondingly reduced. The water vapour atmosphere, however, would quickly cool, and the original ocean

would have contained only a fraction of its present mass. The subsequent, comparatively slow, emission of the bulk of the water from the lower solidifying layer could not have led to any free oxygen, as the temperature of the atmosphere would be too low. If, however, the crust is assumed to solidify from the bottom, it seems justifiable to consider that the bulk of the present ocean water was present in the atmosphere before its final cooling commenced, and that, consequently, one of the necessary conditions for the production of oxygen would be satisfied.

We may, therefore, conclude that the main difficulty in Tammann's theory is the question of the temperature of the outer layers of the postulated water vapour atmosphere, and that, if Milankovitch's views on the conditions in such an atmosphere are correct, then the production of free oxygen by the proposed mechanism is impossible.

(C) The Photochemical Dissociation Theory.

We may now consider the theory of the production of free oxygen by the photo-dissociation of water vapour in the earth's ionosphere, and the subsequent escape of some of the liberated hydrogen due to the apparently high ionospheric temperature. I (8) originally suggested this possibility in 1941, and P. Harteck and J. H. D. Jensen (18) independently put forward the same theory in 1948. I considered that the process would only have been capable of producing enough free oxygen in the course of—say—a thousand million years to enable the main biological reduction of CO_2 to commence. Harteck and Jensen hold that in three thousand million years the process would have produced enough free oxygen to furnish the present amount of atmospheric oxygen about fifty times. I have already pointed out the difficulty of arriving at any approximate figure for the rate of production of free oxygen, owing to our ignorance of the essential quantities even for the present atmosphere. It is easy to see, however, why the two estimates quoted differ so largely. I assumed that the photo-dissociation of water vapour only occurred in the upper F layers of the atmosphere, where the amount of water vapour would be excessively small. Harteck and Jensen, however, consider that the process took place at as low a level as the E layer, and base their conclusion on a careful analysis of the rate of diffusion of water vapour from the troposphere into the E layer and on the available experimental evidence of the kinetics of the H_2O recombination. They also assume that every water vapour molecule, which diffuses into the E layer, is fairly quickly dissociated, and that the resulting hydrogen escapes into space. These assumptions seem questionable, and will be considered more fully later. Personally, I still hold that the known facts of the geochemistry of free carbon make it much more probable that the bulk of the oxygen supply of the earth is derived from CO_2. If geochemists are presented with such a very large evolution of oxygen during geological time, they will have some difficulty in disposing of it. The most plausible explanation would be that the original crustal materials of the earth contained a smaller percentage of oxygen than any igneous rocks now available for chemical analysis; that is that Goldschmidt's estimate of the fossil oxygen, as not more than 2·5 times

the existing amount of atmospheric oxygen, is much too low. It would, thus, appear that the more modest role, which I originally allotted to the photo-dissociation process, is more acceptable from a geochemical point of view.

The position as regards the validity of this photo-chemical theory is, I think, still far from clear. The theory is based on three main assumptions :—

(a) The existence of temperatures exceeding 1000°K., in the upper levels of the earth's atmosphere during geological time in order to allow the escape of the hydrogen at a sufficient rate.

(b) The presence of sufficient water vapour at levels at which the dissociating ultra-violet solar radiation would reach it.

(c) The presence of enough energy in the solar radiation of requisite wave lengths to produce a significant amount of dissociation of water vapour.

I have, already, discussed these points in the previous paper, but in view of more recent knowledge some further information is desirable. It must be emphasised, that only a very incomplete discussion can be attempted, since the number of phenomena capable of throwing light on the problem is so large. To simplify the problem, therefore, I will try to consider the various assumptions, separately, as far as is possible.

(a) *The existence of temperatures exceeding* 1000°*K. in the earth's atmosphere during geological time.*—Bates and Massey (19) summarise our present knowledge of the ionosphere in a simplified representative model, of which the main features are as follows :—

	E layer.
Altitude	120 km.
Gas density	6×10^{12} molecules/c.c.
Temperature	500°K.

	F layer.
Altitude	220 km.
Gas density	10^{11} molecules/c.c.
Temperature	1000°K.

This layer is merged with the F_2 layer at night.

	F_2 layer.
Altitude	300 km.
Gas density	2×10^{10} molecules/c.c.
Temperature	2000°K.

The exosphere can be considered as commencing at some unspecified height above the F_2 layer, and its temperature will fix the rate of escape of any component molecule present in the upper atmosphere. Bates (20) considers that the bulk of the evidence is in agreement with the view that the ionised layers are at high temperatures. The chief contradictory evidence is due to L. Vegard and E. Tonsberg (21). They investigated the rotational structure of the N_2+ bands emitted by aurorae,

and concluded that, even at the summit of auroral streamers at a height of perhaps 200 km., the temperature did not exceed 340°K. Bates, although acknowledgeing that this isolated contradictory evidence is disturbing, still holds that the higher temperature values should be accepted. For a fuller discussion of the evidence, the reader may consult Bates' paper (20).

L. Spitzer (2) has recently discussed the position as regards the temperature of the exosphere. He concludes that it is about 1500°K., and, from considerations based on thermal conductivity, considers that the temperature remains constant from the exosphere down to a level of perhaps 200 Km. The main evidence for the high temperature of the exosphere is based on the escape of helium during geological time. This element must be escaping, since the number of helium atoms present in a column of the atmosphere of cross section 1 cm.^{2} is found by Paneth (22) to be about 5×10^{20}; whereas Lindemann (23) estimates that the corresponding number discharged into the atmosphere during geological time by radioactive rocks is 6×10^{21}. Since the molecular weight of hydrogen is only half that of helium, the evidence that hydrogen, if present in the present exosphere, must escape rapidly, is fairly conclusive.

It would, I think, be rash to conclude from this argument that hydrogen also escaped from the original atmosphere of the earth subsequent to the formation of the ocean, since presumably the chemical composition of the atmosphere was then very different. Its main constituents would, apparently, have been CO_2, N_2, and an amount of water vapour of about the same order as is now present in the atmosphere. It would appear to be impossible to arrive at even approximate figures for the amounts of CO_2 and N_2 present at any epoch, since it depends upon the manner in which these gases were liberated from the crustal materials. If we assume that the bulk of the atmospheric gases were liberated during the solidification of the crustal materials, we can arrive at some approximate figures.

The relevant geochemical data, as determined by Goldschmidt (10), are given in Table 1.

TABLE 1.

	Mass per cm^2 of the surface of the earth ($5 \cdot 10 \times 10^{18}$ cm^2)
Atmospheric nitrogen	755 g.
Atmospheric oxygen	230 g.
Atmospheric carbon dioxide ...	0·4 g.
Atmospheric water vapour ...	3 g.
Oxygen consumed in formation of sediments	256—544 g.
Carbon dioxide consumed in formation of sediments	6·56 kg.
Carbon dioxide consumed in production of free carbon in lithosphere	3·1 kg.

Since both the oxygen and the carbon dioxide, consumed in the formation of the sediments, are supposed to have been derived from the atmosphere, we can arrive at an approximate estimate of the composition of the original atmosphere on the assumption already stated.

TABLE 2.

Original Atmosphere.

	Mass per cm^2 of the earth's surface.
Nitrogen	755 g.
Oxygen	0 g.
CO_2	5·9 kg.
CO_2 dissolved in ocean ...	3·8 kg.
Water vapour	3 g.

In estimating the amount of CO_2 dissolved in the ocean, I have assumed it to be fresh water at a temperature of 10°C., and that its volume was the same as the present ocean I have put down the oxygen as zero on the assumption that Tammann's theory is incorrect It will be seen that this increases the difficulties of the photochemical theory of the origin of free oxygen It is impossible to arrive at a figure for the water vapour content of the postulated atmosphere, but it would probably be not less than the present amount.

The figures given are, naturally, only to be taken as a rough guide to the composition of the original atmosphere It is, I think, justifiable to conclude that it consisted mostly of CO_2 with a certain proportion of nitrogen The problem then arises whether the temperature of the exosphere of such an atmosphere would be sufficiently high to enable hydrogen to escape at a significant rate.

The production and high temperature of the existing ionized layers is generally attributed to certain photochemical reactions Bates and Massey (19) considered that the main reactions are as follows :—

E layer	$h\nu + O_2 - O_2^+ + e.$	$h\nu$ 12·2 e.V.
F and F_2 layers ...	$h\nu + O - O^+ + e.$	$h\nu$ 13·5 e.V.
	$h\nu + N_2 - N_2^+ + e.$	$h\nu$ 15·5 e.V.

Bates (20) has, more recently, ruled out the nitrogen molecule reaction, basing his conclusion on the spectrographic evidence obtained by J. and M. Dufay (24) from the twilight band spectra, which shows that the N_2^+ content of the F layers is minute He considers the only other possible reaction to be :—

$$h\nu + N^+ - N^+ + e. \qquad h\nu \ 14{\cdot}5 \text{ e.V.}$$

It seems to be fairly well established at present that the oxygen molecule is mainly dissociated at heights above 150 km., but any evidence for the dissociation of the nitrogen molecule seems to be inconclusive. Bates, however, considers that it is not unlikely that the nitrogen atom reaction makes some contribution to the formation of the F layers, if considerable dissociation of the upper atmospheric nitrogen

exists. It will, thus, be seen that the ionisation and consequent high temperature of the ionosphere is now considered to be mainly due to the oxygen present. The position as regards the temperature of the existing exosphere is similar. Spitzer (2) attributes its apparent high temperature to the oxygen atoms present.

It will, thus, be seen that even if the view is adopted that the existing exosphere is at 1500°K., it by no means proves that the exosphere of an atmosphere consisting mainly of CO_2 with a proportion of nitrogen would be also at a high temperature. Kuiper (25) thinks that exospheric temperatures on other planets will be similar, if not so extreme as on the earth, even if oxygen is absent from their atmospheres. He bases his conclusion on the fact that most atmospheric gases absorb powerfully below 1800°A. It seems reasonable, therefore, to conclude that nitrogen would in the original atmosphere, have been capable of absorbing the necessary ultra, violet energy required to produce an ionosphere.

There can be very little doubt, however, that the presence of CO_2 in any quantity in the ionosphere and exosphere of a planet must tend to lower their respective temperatures greatly, since CO_2 is capable of radiating in the infra-red. The possible diffusional separation of CO_2 and nitrogen may, however, be important. The molecular weight of CO_2 is 44, that of N_2, 28 and of N, 14. Thus, if it is assumed that above some critical level in the atmosphere, diffusional equilibrium were maintained, and, furthermore, that the nitrogen molecule were dissociated, the percentage of CO_2 present would decrease fairly rapidly with height, so that the upper exospheric layers might consist mainly of nitrogen, and the conditions for the attainment of a high temperature be fulfilled. It is, thus, conceivable that hydrogen would have escaped from the original atmosphere (i.e., the atmosphere after the condensation of the oceans), but it seems likely that its rate of escape would be considerably slower that at present due to the lower exospheric temperature. This is, I consider, not a fundamental objection to the photochemical theory of the production of free oxygen, since, in my view, the proposed mechanism only supplied originally enough oxygen to enable photosynthesis to start. The period of time available for this process is unknown, but there seems no reason to doubt that it might have been of the order of 1000 million years. This point is discussed more fully later.

It is clear, also, that if free oxygen was produced during the early stages of the earth's history in this way, the process must have gone on continuously during the whole of subsequent geologic time, since the presence of free oxygen would apparently favour it. As I have already mentioned, Harteck and Jensen maintain that in 3000 million years the photochemical process would have produced about fifty times as much free oxygen as at present exists. This would mean that the production of oxygen by photosynthesis was quite unimportant, and, as I have already pointed out, would lead to grave geochemical difficulties. It would seem foolish to abandon the photosynthesis process as the main source of free oxygen, since this process can be seen in action, and agrees fairly well with the available geochemical evidence. I think, if it can be definitely proved that Harteck's and Jensen's estimate of the present rate of production of free oxygen is correct, we will be forced to assume that this figure is not applicable to the whole of geologic time, but that the average rate of oxygen production is much lower. Obviously changes in the solar radiation could explain this, but discussion of this possibility seems useless, since very little evidence is available.

(b) *Amount of water vapour present in the upper layers of the atmosphere.*—In the previous paper, I assumed that the atmosphere might be taken to be in diffusional equilibrium above the tropopause, and that the water vapour pressure at the base of the diffusional layer might be taken as the vapour pressure of water at the temperature of the tropopause. Most recent results, however, show fairly conclusively that both these assumptions are incorrect for the existing atmosphere. Direct chemical analysis of stratosphere specimens, taken by means of V2 rockets, show that the percentage composition of air up to a height of 70 km., is unaltered (26). No diffusional separation of even helium could be detected. Furthermore, it is now generally held that the temperature above the tropopause does not rise continuously with height until the temperature of the E layer is reached, but that after an initial rise to a height of about 50 km., the temperature falls to a second minimum at a height of about 80 km. Figures for the " standard atmosphere ", recently specified by the National Advisory Committee on Aeronautics of the U.S.A., (27), are given in Table 3.

TABLE 3.

" Standard Atmosphere ".

Height (Km.)	Temperature °K.	Height (Km.)	Temperature °K.
0	288	60	350
10·8	218	78	240
32	218	83	240
50	350	120	375

These values have been approximately confirmed by V2 rocket research (28). The rocket estimates, however, tend to be lower than N.A.C.A., values, thus the minimum temperature at about 80 km., is found to be 200°K. Even lower values have been advocated: thus, Humphreys (29) claims that the noctilucent clouds, which form at about a height of 82 km., are composed of ice crystals, and that this would involve that the temperature was 160°K., at this height. The vapour pressure of ice at 160°K., is about 10^{-6} mm. of mercury. The total atmospheric pressure at a height of 80 km., is, as determined by V2 Rocket measurements (28), 10^{-2} mm. This shows that, at this height, at least one molecule in 10,000 is a water molecule. Since it seems now probable that no diffusional separation occurs at a height less than 100 km., it would seem correct to conclude that the same proportion of water vapour is present in the existing E layer. It is impossible, however, to estimate the amount of water vapour at a given level above the height where diffusional separation commences, because it depends on the amount of dissociation of the oxygen and nitrogen molecules. Since the molecular weight of water is 18, the percentage water vapour content of an undissociated atmosphere in diffusional equilibrium would increase fairly rapidly with height ($N_2 = 28$. $O_2 = 32$), whereas if the oxygen and nitrogen are all dissociated it would decrease, but not so rapidly ($N = 14$. $O = 16$). We might, accordingly, assume that the actual figure for the F layers would be of the same order as the E layer.

The conditions, however, in an atmosphere consisting mainly of CO_2 would probably be very different. The present temperature distribution, above the tropopause, seems to depend very largely on the presence of oxygen: thus the rise in temperature from 25 to 50 km., is apparently due to O_3. It seems clear that the vapour pressure of water at the minimum temperature reached in any atmosphere will be one of the ruling factors in the distribution of water vapour above that height. In the previous paper I assumed that Gold's and Humphrey's mathematical explanation of the presence of a tropopause in an atmosphere in radiative equilibrium, could be applied to a mixed CO_2 and N_2 atmosphere, and that a rough estimate of the minimum temperature in this atmosphere thus obtained. Unfortunately, meteorologists now consider that the theory is invalid. Thus, Brunt (30) holds that no adequate explanation has been given of either the constancy of the mean lapse rate at all heights in the troposphere or the sudden change at the tropopause. He considers, however, that it can be established that there will be a slow decrease of temperature with height in the lower layers of an atmosphere in radiative equilibrium (*loc. cit.* p. 151). Consequently, if we assume that the upper levels of the mixed CO_2 and N_2 atmosphere were heated by ultra-violet radiation, as occurs in the present atmosphere, there apparently, must have been a tropopause in this atmosphere; but neither its height nor its temperature can be, even roughly, estimated. Thus, it seems impossible to arrive at any quantitative conclusions as to the amount of water vapour available for dissociation under these conditions; hence, no numerical estimate of the original rate of production of oxygen by this method can be made until the general theory of radiative equilibrium has been solved.

(c) *The presence of enough energy in the solar radiation of the requisite wave lengths to produce a significant amount of dissociation of water vapour.*—In discussing this problem, the assumption will be made that the solar radiation has not changed appreciably during the life-time of the earth. This obviously may not be true, but seems to be the best we can do with the knowledge available.

I see no reason to doubt that dissociation of water molecules may occur above a certain height in the present atmosphere. The dissociation energies of oxygen, nitrogen, hydrogen and water vapour, as stated by Mann, Hustrulid and Tate (31), are given in Table 4.

TABLE 4.

$D(O_2)$	$\longrightarrow O + O$	5·09 electron volts
$D(N_2)$	$\longrightarrow N + N$	7·35 ,, ,,
$D(H_2)$	$\longrightarrow H + H$	4·46 ,, ,,
$D(H_2O)$	$\longrightarrow H_2 + O$	5·0 ,, ,,
$D(H_2O)$	$\longrightarrow H + OH$	5·1 ,, ,,
$D(H_2O)$	$\longrightarrow H + H + O$	9·5 ,, ,,
$D(OH)$	$\longrightarrow O + H$	4·4 ,, ,,

From these figures it is clear that, if at any height in the atmosphere oxygen exists mainly in the atomic form, then it is energetically possible that the dissociation of water vapour molecules also occurs. Various estimates of this height, ranging from about 100 to 150 km., have been made. The question of the amount of dissociation of O_2 in the E layer is still uncertain. Harteck and Jensen assume that dissociation of water vapour is complete in this layer, and, consequently, we would infer that the dissociation of oxygen was also practically complete. This disagrees, however, with Bates' and Massey's theory that the formation of the E layer is due to the ionisation of O_2. Furthermore, Harteck and Jensen assume that the dissociation process is $H_2O \longrightarrow H + H + O$. This requires 9·5 electron volts, and, since N_2 is certainly not dissociated in the E layer, seems improbable. This process might, however, take place in two stages, thus :—

$D(H_2O)$	$\longrightarrow$	$H_2 + O$	5·0 e.V.
$D(H_2)$	$\longrightarrow$	$H + H$	4·46 e.V.

On the whole, it seems justifiable to conclude that in the present atmosphere, at heights greater than 150 km., dissociation of water vapour probably takes place. I have already discussed the experimental evidence, mainly due to Rathenau (32), on the short wave absorption bands of water vapour, which also seems to favour this view (8). I think it is reasonable to conclude that if dissociation of water vapour occurs in the present atmosphere at high levels, it would also have occurred in the primitive CO_2 and N_2 atmosphere at some level, provided the nature of the solar radiation was the same as at present.

It, thus, seems impossible to form any quantitative estimate of the rate of production of free oxygen by the photochemical process—even in the existing atmosphere. Jensen and Harteck claim to have solved this problem by estimating on certain assumptions the rate at which water vapour can diffuse from the tropopause to the E layer, and by assuming that the rate of oxygen production corresponds to this value. They have not, however, considered what concentration of hydrogen would be necessary at the base of the exosphere, so that the hydrogen liberated would escape sufficiently rapidly. If we assume that the exosphere is isothermal, as Spitzer considers, and is in diffusional equilibrium, we can from Jeans' approximate results obtain some information on this point. If t_o is the time required for the earth to lose an amount equal to a layer one centimetre thick of any gaseous component at the base of an isothermal, diffusional atmosphere, then according to Jeans :

$$t_o = \frac{4{\cdot}34}{C(1 + 3ga/C^2)} \text{ exp. } 3ga/C^2$$

where C = molecular velocity
a = radius of earth
g = acceleration due to gravity.

Using this formula, I have calculated the number of hydrogen molecules per c.c., required at the base of the exosphere to produce 240 g. of oxygen per cm^2 of the

surface of the earth in 10^9 years and in 6×10^7 years, the latter being approximately Harteck and Jensen's value. The results of this calculation are given in Tables 5 and 6.

Table 5 refers to molecular hydrogen H_2 and Table 6 to atomic hydrogen H_1. It seems justifiable to consider that the total number of all kinds of gas molecules per c.c., at the base of the exosphere cannot exceed that in the F layer, i.e., about 10^{11} molecules per c.c. In the fourth column, the relative concentration of either hydrogen molecules or atoms at the base of the exosphere is given, assuming the total concentration has this maximum value.

TABLE 5.

T.	θ	N	N/10^{11}
10^9	500	8×10^{15}	
,,	1000	10^9	$1/10^2$
,,	1500	7×10^6	$1/1{\cdot}4 \times 10^4$
6×10^7	500	$1{\cdot}3 \times 10^{17}$	
,,	1000	$1{\cdot}7 \times 10^{10}$	$1/5{\cdot}9$
,,	1500	$1{\cdot}1 \times 10^8$	$1/9{\cdot}1 \times 10^2$

Table 5 refers to diatomic hydrogen.

TABLE 6.

T.	θ	N	N/10^{11}
10^9	500	$1{\cdot}5 \times 10^9$	1/67
,,	1000	5×10^5	$1/2 \times 10^5$
,,	1500	6×10^4	$1/1{\cdot}7 \times 10^6$
6×10^7	500	$2{\cdot}5 \times 10^{10}$	1/4
,,	1000	8×10^6	$1/1{\cdot}2 \times 10^4$
,,	1500	10^6	$1/10^5$

T = time in years required to produce 240 g., of oxygen per cm.^{2} of surface of earth.

θ = Temperature of exosphere in °K.

N = number of either hydrogen molecules or atoms per c.c., at base of exosphere.

Table 6 refers to monatomic hydrogen.

No estimate of the actual concentration of hydrogen in the atmosphere above the F layer can be made at present. Some evidence may be obtained from the spectar of the night sky and aurora. According to P. Swings (33), no atomic lines of hydrogen are present in the spectrum of the night sky, and the molecule bands of H_2 cannot be identified with any certainty. The Balmer lines (Hα, Hβ, Hγ) occur, however, in the spectra of some aurorae. The probability seems to be that the concentration of hydrogen must be low, at least up to heights of about 300 km., but the usual difficulty of the problem of excitation conditions naturally may affect this conclusion. If we assume that only one molecule in 10^4 is hydrogen, we see from Tables

5 and 6 that for monatomic hydrogen, the temperature of the exosphere must exceed about 900°K., for Harteck and Jensen's rate of oxygen production to be reached; and that for diatomic hydrogen, a temperature of even 1500°K., would not give this rate. Since, however, these authors consider that the hydrogen is monatomic, and since the exosphere temperature probably is about 1500°K., there seems to be no reason to doubt their conclusions on these grounds.

Harteck and Jensen's assumed value of the tropopause water vapour pressure seems, however, to be unduly high, and, since the rate of diffusion of water vapour into the E layer is supposed to depend directly on this value, its reduction would produce a similar decrease in the rate of oxygen production. They assume that the air just above the tropopause is supersaturated, so that the relative humidity is about 150%, and the actual water vapour pressure about 0·045 mm. Experimental work by Dobson and others (34) on the temperature and frost point in the neighbourhood of the tropopause over England seem, however, to show that the lower stratosphere is surprisingly dry. Thus, Shellard (35) gives the average yearly tropopause temperature as 224°K., and the frost point 214°K. This means that the actual vapour pressure would be about 0·0095 mm., and the relative humidity about 30%. Furthermore, the frost point continues to fall rapidly above the tropopause; thus, at a height at which the pressure is 75 millibars below the tropopause pressure, the average yearly temperature is 227°K., and the frost point 198°K., giving a vapour pressure of about 0·0015 mm., and a relative humidity of 3%. If similar conditions apply to the earth's atmosphere as a whole, it would seem that Harteck and Jensen's figure for the rate of oxygen production may be too high by a factor of about thirty.

On the whole, it would seem reasonable to conclude that the photo dissociation of water vapour is not the main source of oxygen in the present atmosphere, but may have supplied the original oxygen necessary to start photosynthesis.

If this view is correct, the atmosphere of the earth, previous to the start of photosynthesis, must have been very different in composition from the present atmosphere, since it contained large quantities of CO_2 and, presumably, only a small amount of free oxygen. R. T. Chamberlin (36), however, considered that the climatic and atmospheric conditions of the earth in early geologic time were not very different from those of later geologic history. He based this conclusion on the evidence of important glaciation in very ancient rocks, and also on the existence of extensive highly oxidised iron ores in Archean strata. He concludes that an Ice Age could not have occurred if the atmosphere contained any large quantity of CO_2, due to its so-called greenhouse effect, and that the formation of the Archean iron ores shows that atmospheric oxygen was plentiful. Up to the present there is however, no generally accepted explanation of the cause of Ice Ages. The effect of small changes of the percentage of CO_2 in the atmosphere as an effective cause is generally discounted, since the heat absorption of the water vapour normally present is so much more important than that of the CO_2. Furthermore, the present amount of CO_2 absorbs practically all the energy radiated by the earth within the limits of its absorption bands. This is shown by the investigation of the reflected earth shine from the Old Moon. Increasing the amount of CO_2 considerably would widen these bands and, possibly, prevent Ice Ages, but it is not clear that it must inevitably

do so. Sir George Simpson (37) holds that the Pleistocene Ice Age cannot be explained by any change located in the earth itself, but must be due to changes outside the earth. He attributes it to fluctuations in the intensity of the solar radiation, and, thus, explains the general structure of the Pleistocene Ice Age with its interglacial periods. If his theory is accepted for the recent Ice Age, it would seem logical to hold that previous Ice Ages had been produced by similar effects, and might occur even if the atmosphere contained large quantities of CO_2.

Some confusion may, however, have arisen from Chamberlin's use of the expression 'geologic time', since he held that atmospheric oxygen was mainly produced by photosynthesis, it is clear that he also believed that the atmosphere was different in composition before the start of this process, and that he intended geologic time to apply only to subsequent periods. The point of interest is, whether any geological evidence can be obtained as to the approximate length of these periods, Various estimates of the age of the earth have been made, and up to recently a figure of about 2000 million years was generally accepted. Holmes (38), and others have increased this figure to about 3000 million, basing their conclusions on the isotopic constitution of lead ores; but Jeffreys (39) still considers that the lower figure is more likely to be correct. On the whole, it would appear that the age of the earth is probably not less than 2500 million years. Abundant fossil remains first appear in Cambrian rocks of age about 500 million years, but life must have originated at a much more remote epoch. A. C. Lane (40) has put forward the view that the atmosphere of Keewatin and early Huronian times contained very little free oxygen, basing his conclusion on a study of the Pre-Cambrian rocks of the Great Lake Area. He considers that the chemical nature of the Keewatin Greenstone Schists shows that they were formed in an atmosphere with little free oxygen, whereas the highly oxidised great iron series of the Upper Huronian shows that free oxygen had then become plentiful. A. MacGregor (41) has also pointed out the low oxidation of the Rhodesian early Pre-Cambrian rocks, and attributed it to the same cause. If Lane's theory is accepted, it involves that photosynthesis must have commenced on a large scale at about the time of the Laurentian orogenesis, i.e., about 1100 million years ago: thus, for about half the life-time of the earth the atmosphere must have been largely composed of CO_2 with very little oxygen, corresponding, apparently, to the existing atmosphere of Venus.

It, thus, appears that a period of the order of a 1000 million years is available for the initial production of oxygen by photo-dissociation of water vapour. During this period, some of the free oxygen produced would probably have been consumed in the oxidation of sedimentary rocks and a steady state may have been reached in which the production and consumption of oxygen were equal, and the amount of free oxygen in the atmosphere small. On this view, the atmospheric conditions necessary for the start of photosynthesis would have persisted during most of geological time. On Tammann's theory, however, the amount of oxygen in the atmosphere would have decreased continuously till photosynthesis commenced, so that after a certain period it might have been impossible for photosynthesis to start, and, perhaps, on this ground the photo-dissociation theory is more attractive. The two theories are not mutually exclusive, so that either or both proposed mechanisms may have been effective.

Summary.

The composition of the earth's atmosphere before the formation of the ocean is discussed, and it is shown that recent theories on its origin confirm the view that it contained no free oxygen. The various mechanisms which have been put forward to explain the subsequent production of free oxygen are considered, and it is concluded that, although free oxygen has been mainly produced from CO_2 by photosynthesis, some non-biological process of oxygen production is necessary to enable the former process to start. A discussion of Tammann's thermal dissociation theory and the author's and Harteck and Jensen's photo-dissociation theory is then given. It is shown that although the period between the solidification of the crust and the formation of the ocean must have been short, this is not a fundamental objection to Tammann's theory if an isothermal atmosphere is assumed.

On the other hand, if Milankovitch's views on the temperature gradient in the atmosphere during this period are correct, Tammann's theory must be invalid. A discussion of the photo-dissociation theory follows, in which it is concluded that, while in a qualitative sense the theory is probably sound, it is impossible to arrive at quantitative results at present. Harteck and Jensen's estimate of the rate of production of oxygen by this process is considered to be excessive both on geochemical grounds and also from the fact that recent experimental measurements show that the air in the neighbourhood of the tropopause is surprisingly dry. The paper concludes with some geological evidence of the absence of free oxygen from the atmosphere during a considerable part of the earth's lifetime.

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